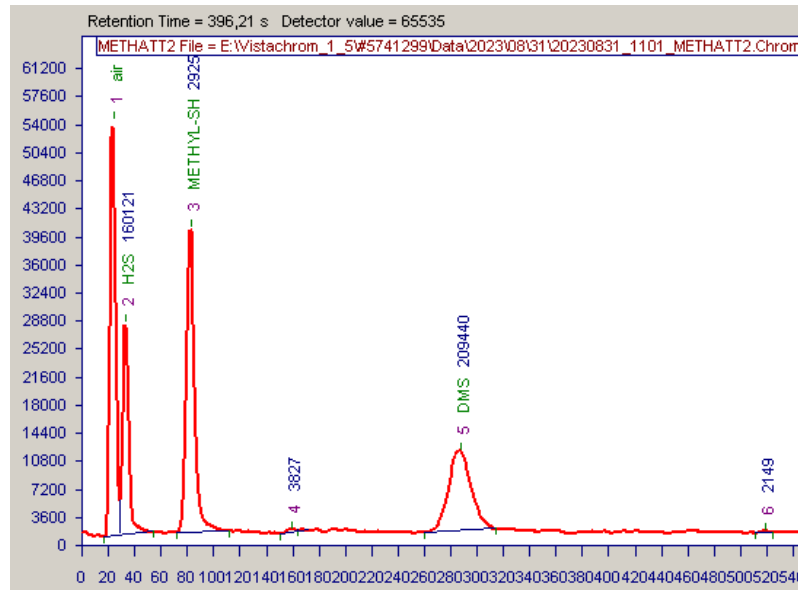


Calibrate a GC

Advices and good practices

Why the calibration is required ?

- Be sure of the identification of the molecules
- Know the relation between “Peak area” and “Concentration”



- Follow the sensitivity of an instrument over a period of time
- Be sure the quantification will be good in the next sample cycles

Calibration gas to be used

Different span gas can be used :

- Molecules coming from permeation tubes, flushed with neutral gas (N_2 or Zero air)

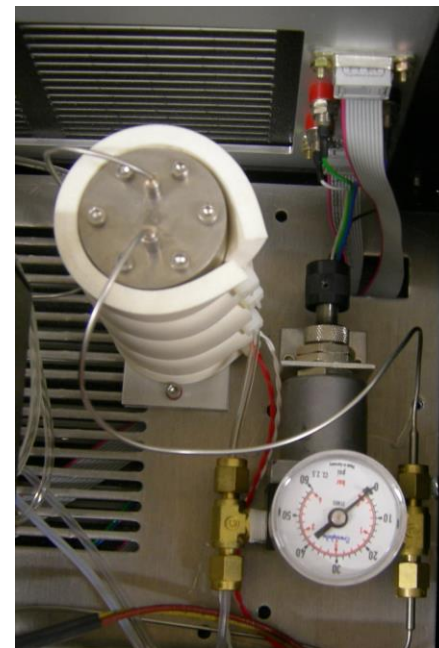


- Calibration gas contained in a calibration cylinder



Calibration : good habits

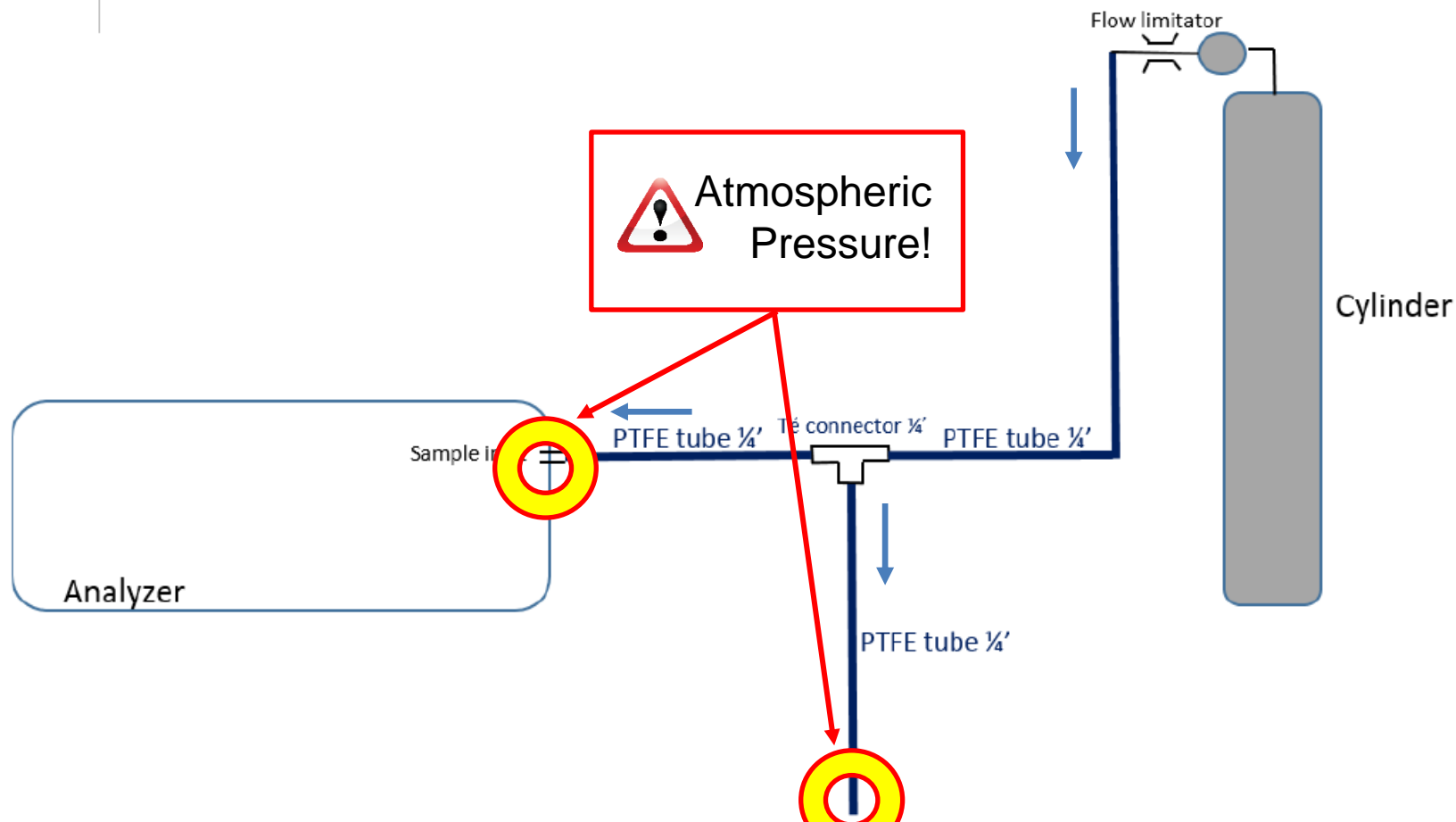
- Calibration gas at ambient pressure for most applications
- Purge your cylinder, pressure regulator and tubes 3 times before connecting the GC
- Try to use always the sample pressure regulator and tube, connected to one calibration cylinder
- Take your time to have stable calibration results :
 - Check that the integration of the peaks is good
 - Check the stability of peaks areas on several cycles
- The calibration cylinder has to be located :
 - In the same room
 - At the same temperature
 - No “cold point” on the tubes!
 - Cylinder located as close as possible to the GC



Calibrate with a cylinder

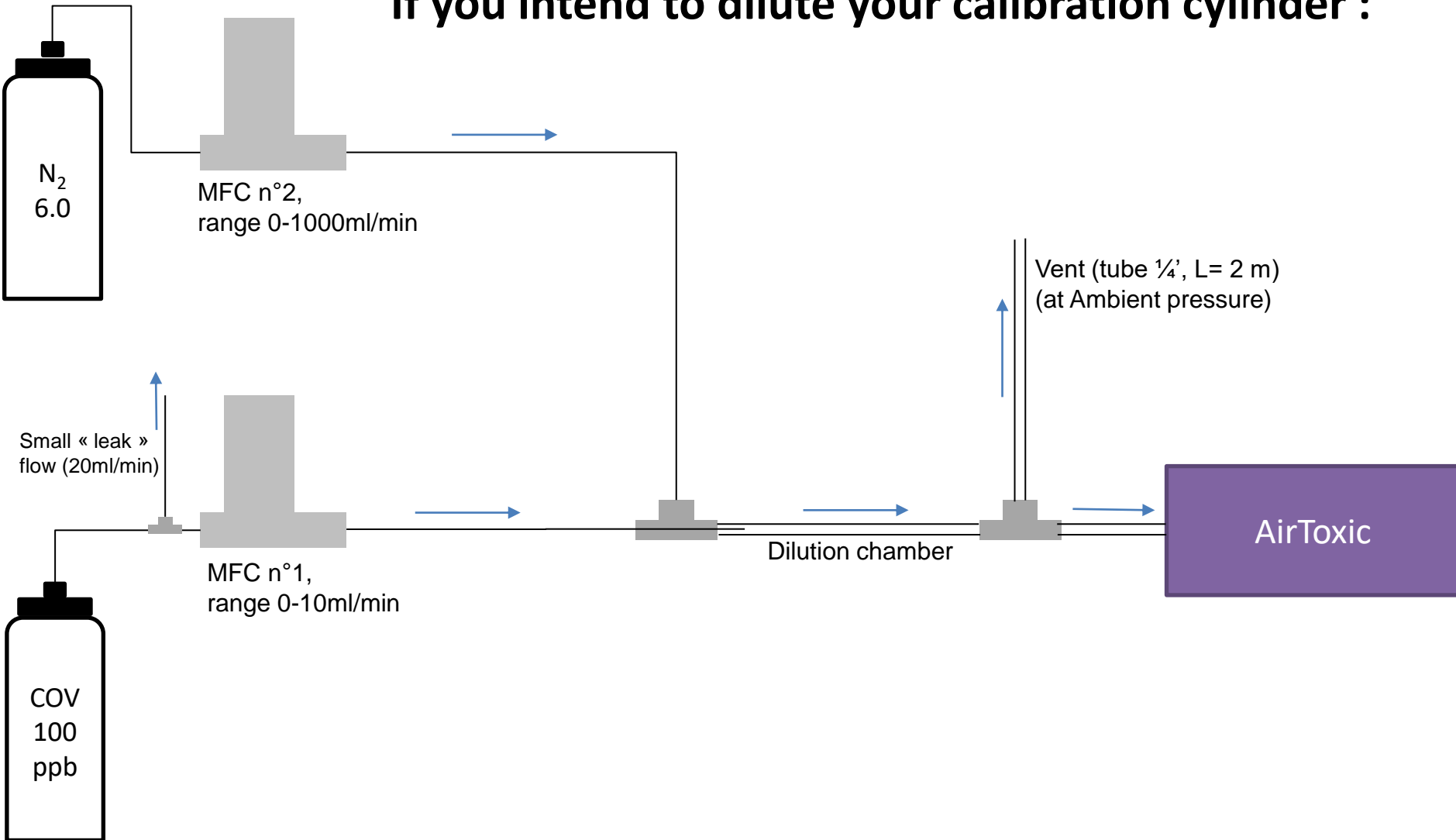
How to connect the external calibration cylinder?

- To obtain good results
- To protect your instrument and not create damages
- Calibration gas concentration written on the cylinder certificate



Calibrate with a cylinder

If you intend to dilute your calibration cylinder :



Calibrate with permeation tubes

How to connect a permeation oven containing permeation tubes

- Permeation oven flushed with neutral gas : N_2 or « zero air »

Internal permeation oven :

Nothing to do, just select the « calibration » method from Vistachrom



External permeation oven :

Connect the oven « outlet mixture » to the GC « sample inlet »



- The calibration gas ALWAYS has to be at ambient pressure
- Required : check the flow crossing the oven with a good precision

Calibrate with permeation tubes

Using a permeation tube :

- Permeation rate written on the tube certificate (ng/min at ...°C)
- Permeation oven gas flows measured (mL/min)
- To know the concentration of your calibration gas at the oven outlet :

$$C_{mg/m3} = \frac{\text{permeation rate}}{\text{Flow}}$$

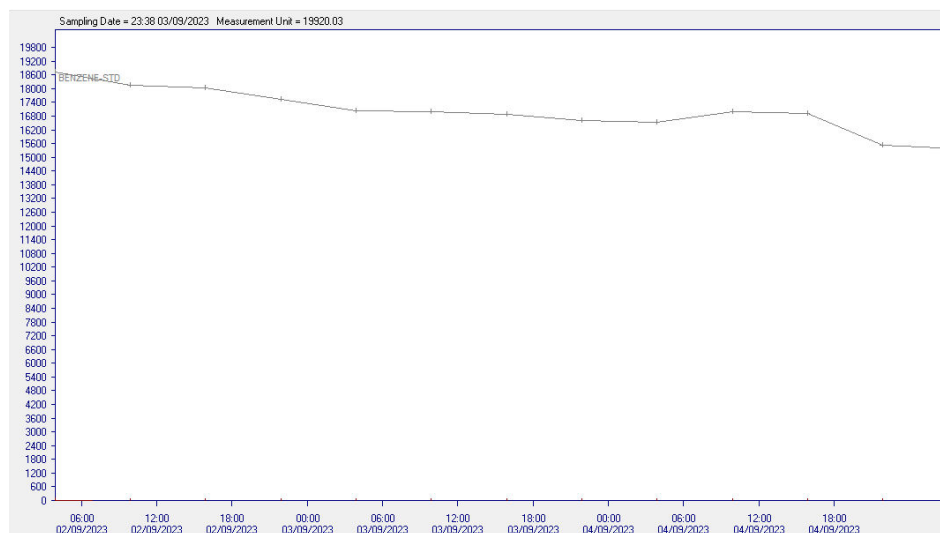
Parameter	Unit	Name	Remark
Permeation rate	ng/min	Permeation rate	Rate written on the tube
Flow	mL/min	Flow crossing the permeation oven	



Base Sensitivity definition

“BS” is a Chromatotec parameter :

- To know how sensitive an instrument is
- Follow the sensitivity of one instrument over time

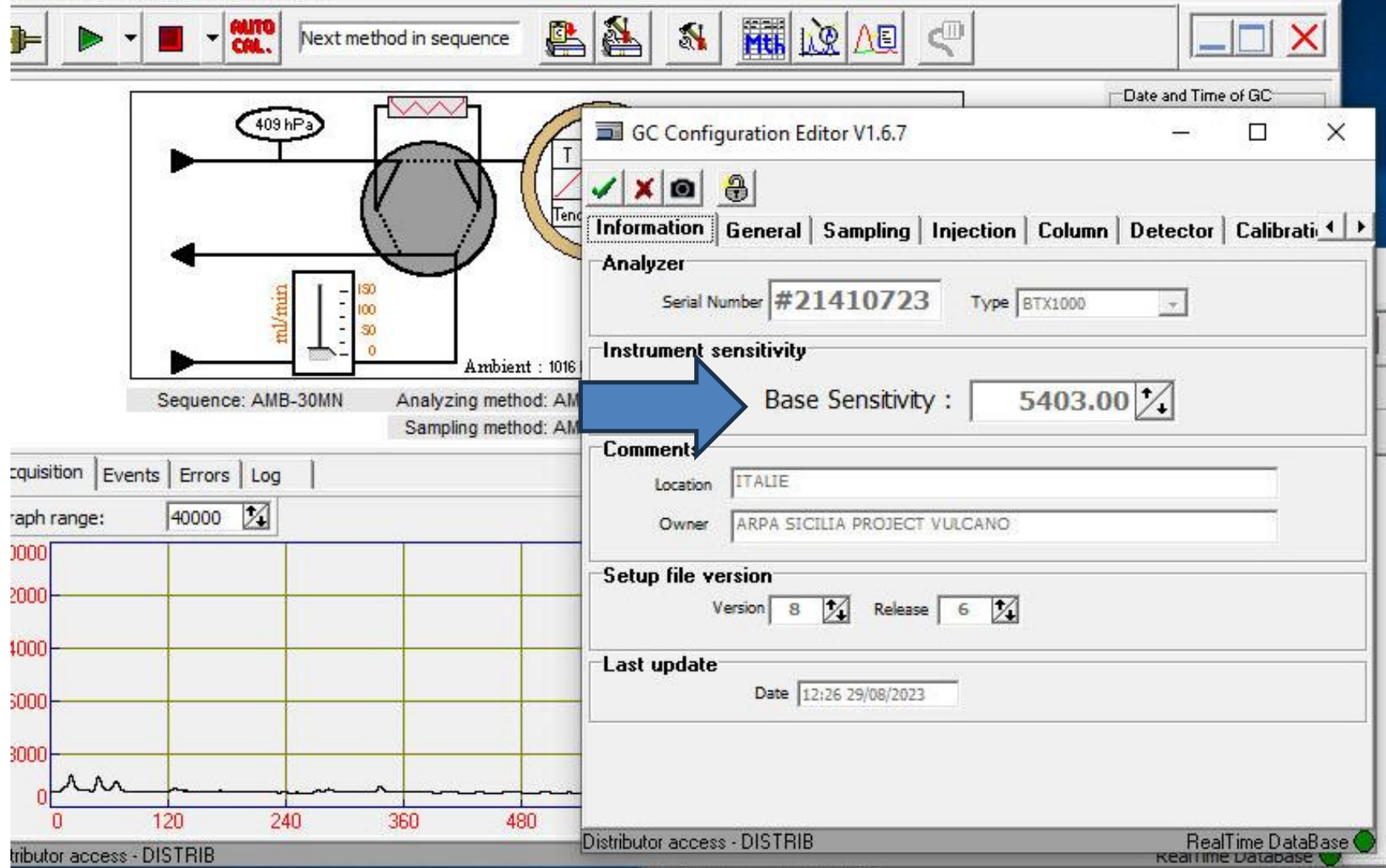


- Required only one molecule to be update during a calibration process
- BS is updated or checked during a calibration process, focusing on a “reference compound” : Benzene or DMS.
- In “routine mode”, BS is used by the software to calculate the concentrations of all the molecules.

Base Sensitivity definition

21410723 - airmoBTX-STD - Vistachrom V1.6.7 - (FW:8.6 - 0x4A89)

Instrument Display Main Window



The screenshot displays the Vistachrom V1.6.7 software interface. The main window shows a gas chromatography (GC) schematic diagram with a pressure of 409 hPa, a flow rate of 150 mL/min, and an ambient temperature of 1016. Below the diagram, the sequence is AMB-30MN, the analyzing method is AM, and the sampling method is AM. A blue arrow points from the 'Base Sensitivity' field in the 'Instrument sensitivity' section of the 'GC Configuration Editor V1.6.7' window to the value 5403.00. The 'GC Configuration Editor' window has tabs for Information, General, Sampling, Injection, Column, Detector, and Calibration. The 'Information' tab is active, showing the analyzer serial number #21410723 and type BTX1000. The 'Instrument sensitivity' section shows the 'Base Sensitivity' set to 5403.00. The 'Comments' section includes fields for Location (ITALIE) and Owner (ARPA SICILIA PROJECT VULCANO). The 'Setup file version' section shows Version 8 and Release 6. The 'Last update' section shows the date 12:26 29/08/2023. The bottom status bar indicates 'Distributor access - DISTRIB' and 'RealTime DataBase'.

GC Configuration Editor V1.6.7

Information General Sampling Injection Column Detector Calibration

Analyzer
Serial Number #21410723 Type BTX1000

Instrument sensitivity
Base Sensitivity : 5403.00

Comments
Location ITALIE
Owner ARPA SICILIA PROJECT VULCANO

Setup file version
Version 8 Release 6

Last update
Date 12:26 29/08/2023

Distributor access - DISTRIB RealTime DataBase

Base Sensitivity definition

For a GC having a sampling loop :

Models : TRS Medor, EnergyMedor, ChromaFID, ChromaPID, ChromaTCD...

$$BS = \frac{RF \cdot Area}{C}$$

Parameter	Unit	Name	Remark
BS	au/(mg/m ³)	Base Sensitivity	BS is used to know the sensitivity of an instrument
RF	None	Response Factor	RF is a constant value, displayed in the substance table, for each chemical compound
Area	au	Area below a peak	Area displayed below each peak on a chromatogram
C	mg/m ³	Concentration	

Once the BS is calculated, the same formula can be used to calculate the concentrations of the other compounds:

$$C = \frac{RF \cdot Area}{BS}$$

Base Sensitivity definition

Response Factors (RF) are listed in the “substance tables” :

Edit substances table

Substances table information

Substances table name: Author:

For the analyzer serial number: Analyzer type:

Substances table

#	Name	RT Min	RT Max	Select Peak	GC Result formula	With X=
1	BENZENE	268	278	Middle	X	Area/BS
2	CYCLOHEXANE	290	300	Middle	1.1 * X	Area/BS
3	TOLUENE	560	570	Middle	1.05 * X	Area/BS
4	ETHYLBENZENE	761	771	Middle	1.1 * X	Area/BS
5	M&P-XYLENES	773	783	Middle	1.1 * X	Area/BS
6	STYRENE	797	807	Middle	1.1 * X	Area/BS
7	O-XYLENE	807	817	Middle	1.1 * X	Area/BS

- RF are optimized by Chromatotec
- RF are verified using calibration mixtures

No need to adjust them frequently for instruments having a “stable detector” : FID, PID, ...

Base Sensitivity definition

For a GC having a sampling trap :

Models : AirmoVOC, AirmoBTEX, AirToxic, Airmozone, AirmoS...



$$BS = \frac{RF.Area}{C.V}$$

Parameter	Unit	Name	Remark
BS	au/ng	Base Sensitivity	BS is used to know the sensitivity of an instrument
RF	None	Response Factor	RF is a constant value, displayed in the substance table, for each chemical compound
Area	au	Area below a peak	Area displayed below each peak on a chromatogram
C	mg/m3	Concentration	
V	mL	Volume sampled through the trap	V is displayed for each chromatogram, in PeakList

Once the BS is calculated, the same formula can be used to calculate the concentrations of the other compounds:

$$C = \frac{RF.Area}{BS.V}$$

Example of BS calculation : airmoBTEX

Information and operating conditions

Analyser :

Serial Number : #21410723
Owner : ARPA SICILIA PROJECT VULCANO
Location : ITALIE

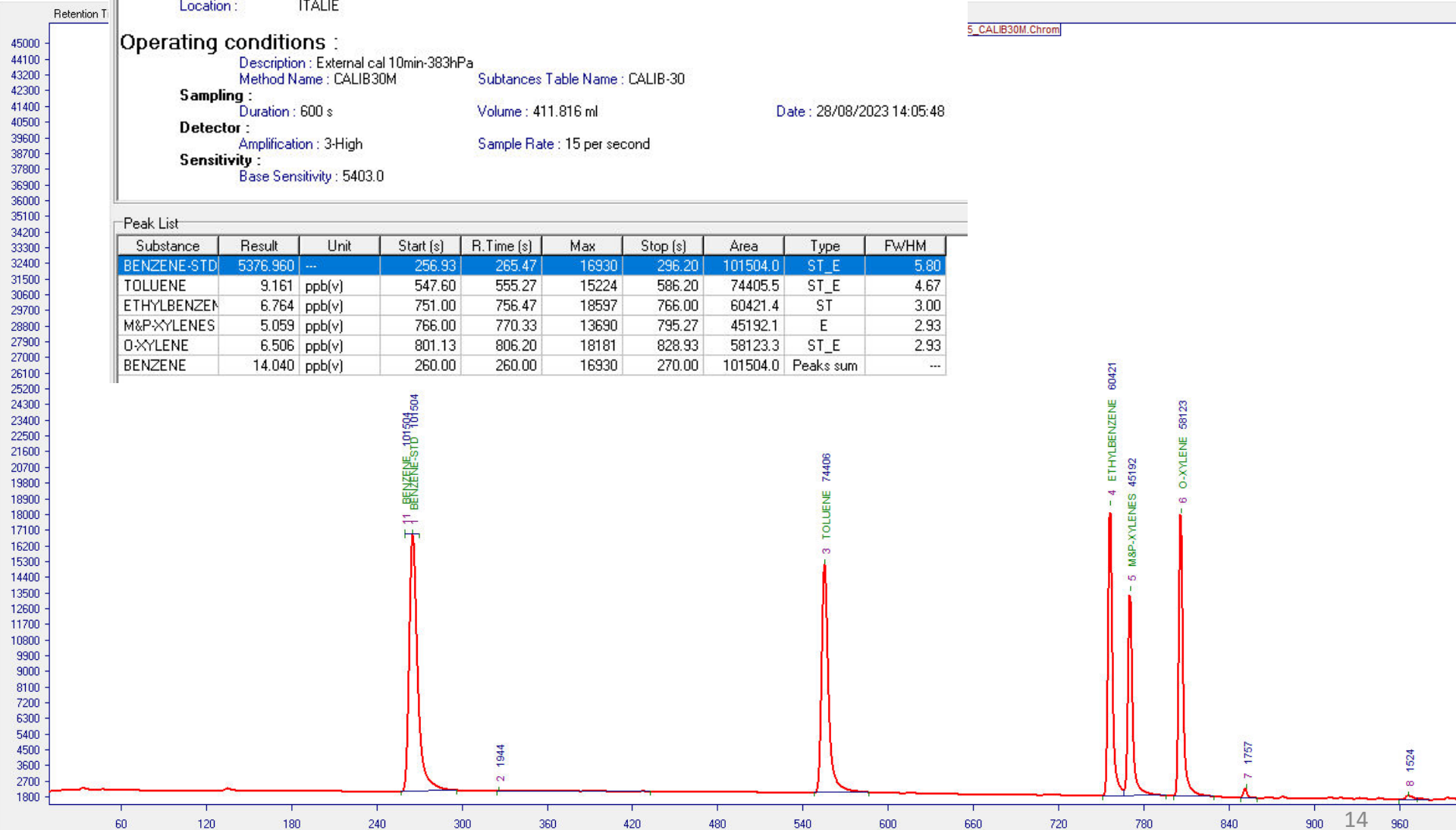
Operating conditions :

Description : External cal 10min-383hPa
Method Name : CALIB30M Substances Table Name : CALIB-30
Sampling : Duration : 600 s Volume : 411.816 ml Date : 28/08/2023 14:05:48
Detector : Amplification : 3-High Sample Rate : 15 per second
Sensitivity : Base Sensitivity : 5403.0

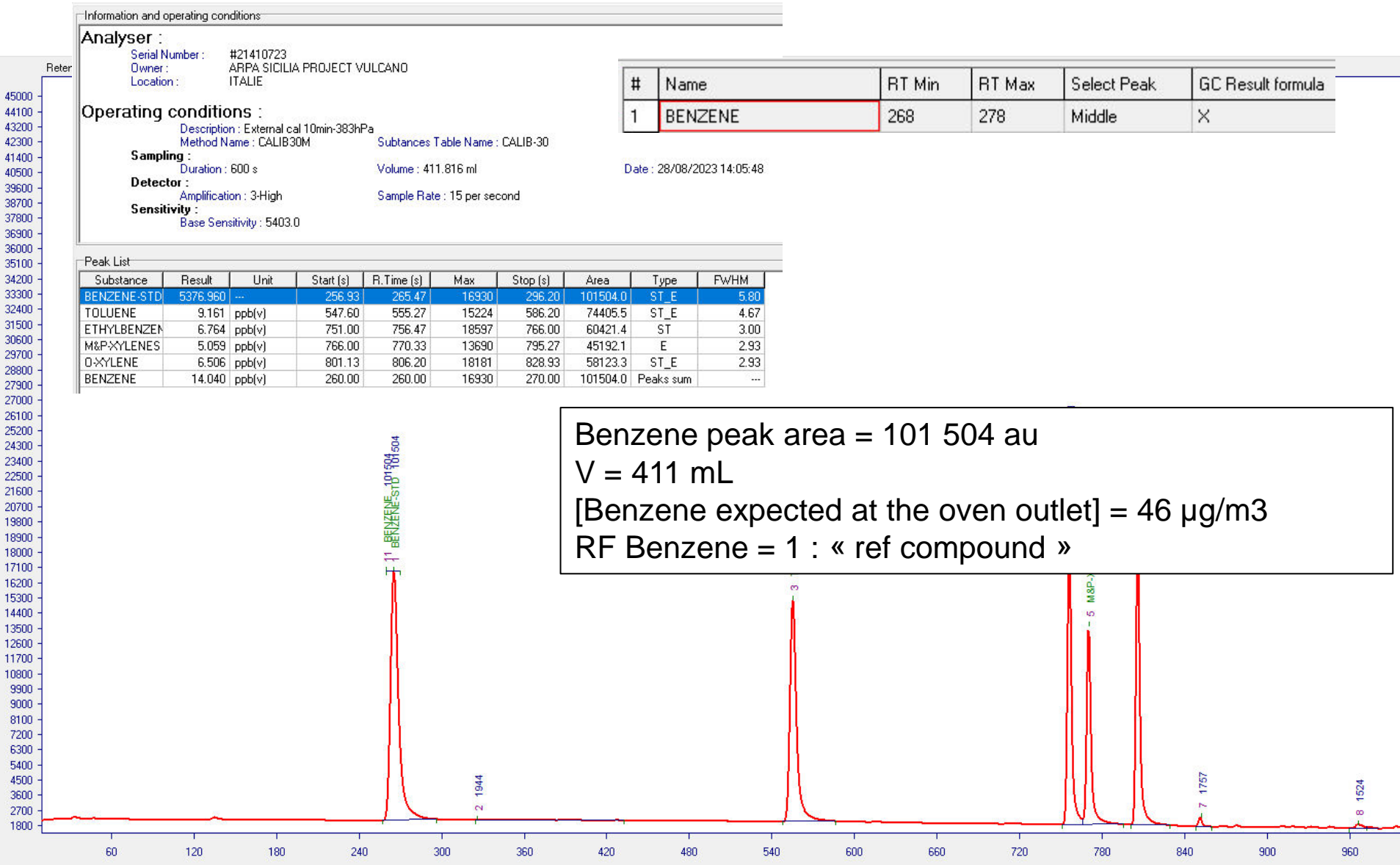
5_CALIB30M.Chrom

Peak List

Substance	Result	Unit	Start (s)	R.Time (s)	Max	Stop (s)	Area	Type	FwHM
BENZENE-STD	5376.960	---	256.93	265.47	16930	296.20	101504.0	ST_E	5.80
TOLUENE	9.161	ppb(v)	547.60	555.27	15224	586.20	74405.5	ST_E	4.67
ETHYLBENZEN	6.764	ppb(v)	751.00	756.47	18597	766.00	60421.4	ST	3.00
M&P-XYLENES	5.059	ppb(v)	766.00	770.33	13690	795.27	45192.1	E	2.93
O-XYLENE	6.506	ppb(v)	801.13	806.20	18181	828.93	58123.3	ST_E	2.93
BENZENE	14.040	ppb(v)	260.00	260.00	16930	270.00	101504.0	Peaks sum	---



Example of BS calculation : airmoBTEX



Example of BS calculation : airmoBTEX

Information and operating conditions

Analyser :

Serial Number : #21410723
Owner : ARPA SICILIA PROJECT VULCANO
Location : ITALIE

Operating conditions :

Description : External cal 10min-383hPa
Method Name : CALIB30M Substances Table Name : CALIB-30

Sampling : Duration : 600 s Volume : 411.816 ml

Detector : Amplification : 3-High Sample Rate : 15 per second

Sensitivity : Base Sensitivity : 5403.0

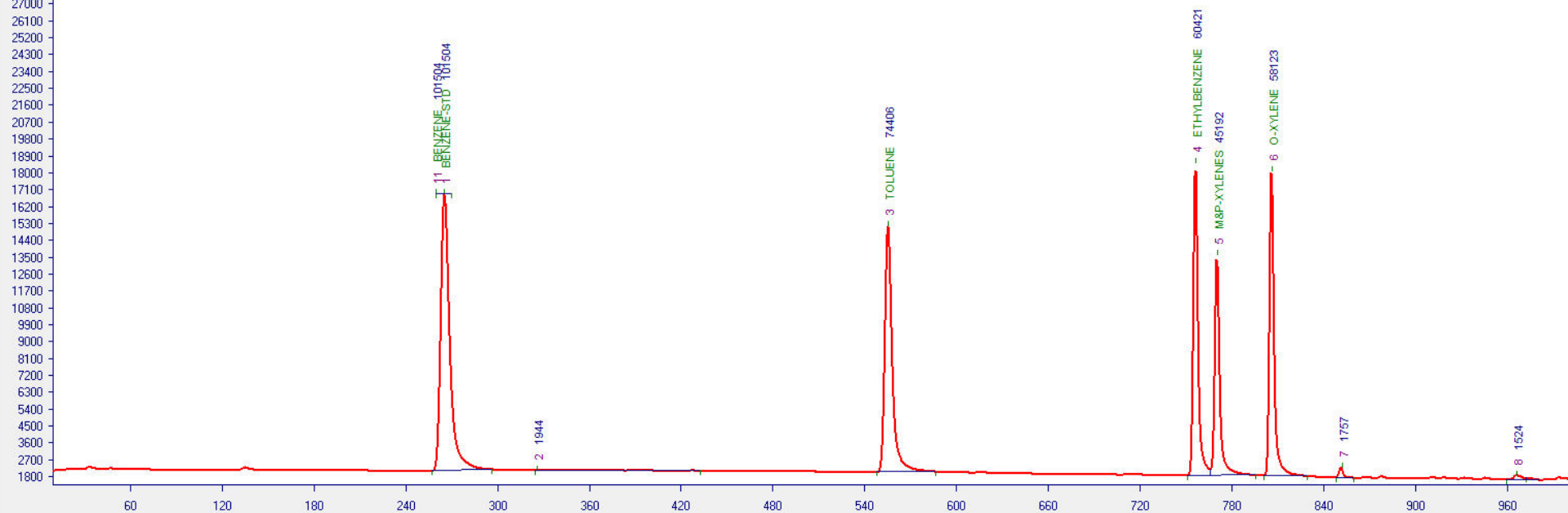
Date : 28/08/2023 14:05:48

#	Name	RT Min	RT Max	Select Peak	GC Result formula
1	BENZENE	268	278	Middle	X

Peak List

Substance	Result	Unit	Start (s)	R.Time (s)	Max	Stop (s)	Area	Type	FWHM
BENZENE-STD	5376.960	---	256.93	265.47	16930	296.20	101504.0	ST_E	5.80
TOLUENE	9.161	ppb(v)	547.60	555.27	15224	586.20	74405.5	ST_E	4.67
ETHYLBENZEN	6.764	ppb(v)	751.00	756.47	18597	766.00	60421.4	ST	3.00
M&P-XYLENES	5.059	ppb(v)	766.00	770.33	13690	795.27	45192.1	E	2.93
O-XYLENE	6.506	ppb(v)	801.13	806.20	18181	828.93	58123.3	ST_E	2.93
BENZENE	14.040	ppb(v)	260.00	260.00	16930	270.00	101504.0	Peaks sum	---

$$BS = \frac{1 \times 101\,504}{0,046 \times 411} = 5\,368$$



Example of BS calculation : airmoBTEX

- To calculate the BS automatically:

File Display Help

#21410723

LAST FILES

Trend Chromato 3D Chromato Peaks List Substances Table Post-Process Quality Control

laboSAV

Ref. Standard: BENZENE Molar Volume: 24.04 dm³

Reference for zero method: CALIB30M Unit GC: ng

Use: Sampled volume from chromat file

CALIB30M

Parameters	BENZENE	TOLUENE	ETHYLBENZ	M&P-XYLEN	O-XYLENE
PEAK AREA	--	--	--	--	--
Minimum (au)	101504	74406	60421	45192	58123
Maximum (au)	101504	74406	60421	45192	58123
Measurement number	1	1	1	1	1
Average (au)	101504	74406	60421	45192	58123
Std. deviation (au)	0.00	0.00	0.00	0.00	0.00
Rel. std. deviation (%)	0.00	0.00	0.00	0.00	0.00
SAMPLING VOLUME	--	--	--	--	--
Minimum (ml)	411.816	411.816	411.816	411.816	411.816
Maximum (ml)	411.816	411.816	411.816	411.816	411.816
Measurement number	1	1	1	1	1
Average (ml)	411.816	411.816	411.816	411.816	411.816
Std. deviation (ml)	0.00	0.00	0.00	0.00	0.00
Rel. std. deviation (%)	0.00	0.00	0.00	0.00	0.00
SAMPLED WEIGHT	--	--	--	--	--
Std. Comp. Concentration (ppm)	0.01	0.01	0.01	0.01	0.01
Comp. Molecular Weight (a.m.u)	78.11	106.17	106.17	106.17	106.17
Sampled mass (ng)	18.974	12.822	12.331	10.822	
Base sensitivity	5349.740	5455.999	4712.274	3664.898	5371.087
Experimental factor	1.000	0.981	1.135	1.460	0.996
RETENTION TIME	--	--	--	--	--
Minimum (s)	260.0	555.3	756.5	770.3	806.2
Maximum (s)	260.0	555.3	756.5	770.3	806.2
Measurement number	1	1	1	1	1
Average (s)	260.0	555.3	756.5	770.3	806.2
Standard deviation (s)	0.000	0.000	0.000	0.000	0.000
Rel. Std. deviation (%)	0.00	0.00	0.00	0.00	0.00

Standards List

laboSAV

Substances	Concentration in bottle (ppm)	Molecular weight (a.m.u)
BENZENE	0.01418	78.11
TOLUENE	0.00864	92.14
ETHYLBENZENE	0.00705	106.17
M&P-XYLENES	0.00678	106.17
O-XYLENE	0.00595	106.17

Substance Add Ins Del

« Auto-Cal » Function

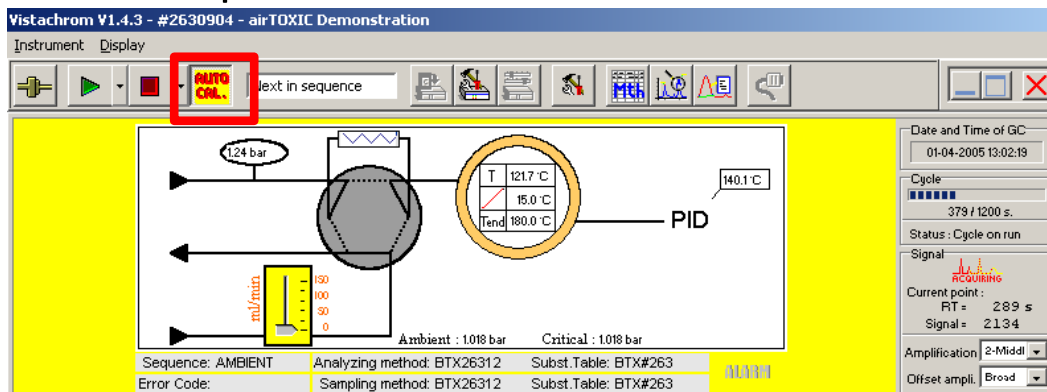
How to use the « Auto-Cal » option?

- Write the expected calibration gas concentration in the calib substance table :

#	Name	RT Min	RT Max	Select Peak	GC Result formula
1	BENZENE-STD	48	58	Middle	Area/[0.12*[SampleVol]]
2	TOLUENE	155	165	Max	1.18*(Area/BS)
3	ETHYLBENZENE	259	269	Middle	1.45*(Area/BS)
4	M&PXYLENES	269	279	Middle	1.11*(Area/BS)
5	OXYLENE	294	304	Max	1.4*(Area/BS)
6	BENZENE	48	58	Sum	Area/BS

Concentration of the standard in mg/m³
(0.12 mg/m³)

- The « Auto-Cal » option must be ON:



Let's practice!



For advanced users

For « non-lineare » instruments / AutoCal

Auto-Cal option on AirToxic

- As the Benzene response formula is not linear :

Substances table information

Substances table name: Author:

For the analyzer serial number: Analyzer type:

#	Name	RT Min	RT Max	Select Peak	GC Result formula	With X=
1	BENZENE-STD	104	114	Middle	$X / (0.0483 * [SampleVol])$	Area
2	BENZENE	104	114	Sum	$1.1 * X^{0.9}$	Area/BS

Curve response of detector

Linear Auto-Calibration

X / Conc.

With X = Area + AreaOfs

Name	Value
Conc.	0.0483
AreaOfs	0
Average point N=	1
Min BS	3000
Max BS	55000

- An Excel files helps for the calculations of the « target C »:

	A	B	C	D	E	F	G	H	I	J	K
1	Calculation of $C_{1,corr}$										
2		$C_{1,real}$	Volume sampled during a CALIBRATION	$C_{1,corr}$							
3		$\mu\text{g}/\text{m}^3$	mL	$\mu\text{g}/\text{m}^3$							
4		49,95	98,85	53,65							
5											
6	Molar volume (L/mol)	24,04									
7	Molecular weight (g/mol)	78,11									
8	Concentration $C_{1,corr}$ in ppb(v)	15,37		16,51							

Auto-Cal option on AirToxic

Calculate the corrected concentration ($C_{1,cor}$) of your standard (in mg/m³) and enter the new value into the calibration substance table.

$$C_{1,cor} = \frac{1}{V} * \sqrt[b]{\left(\frac{C_{1,real} * V}{a}\right)}$$

$C_{1,cor}$: corrected concentration in mg/m³

$C_{1,real}$: real concentration in mg/m³ ; [Permeation rate (ng/min) / Dilution Flow (mL/min)]

V : Sampled volume

$b = 0.9$

$a = 1.1$

Check [EASY CALIB airTOXIC Calib A73022 & A76022-UK 102020.pdf](#) to replace the corrected concentration in the substance table.

Diluting system to be used for this test

Description of the diluted system required to start the linearity test (cf norm):

“For applied concentrations, the relative uncertainty from a dilution ratio to another must be less than 1.5%.”

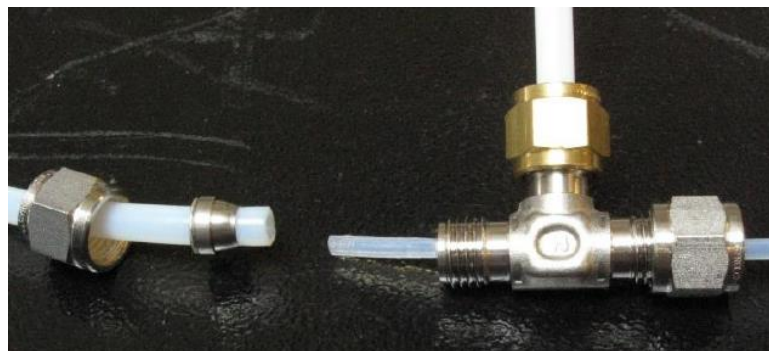
Important remarks:

It is very difficult to be sure the dilutor used fulfills this requirement :

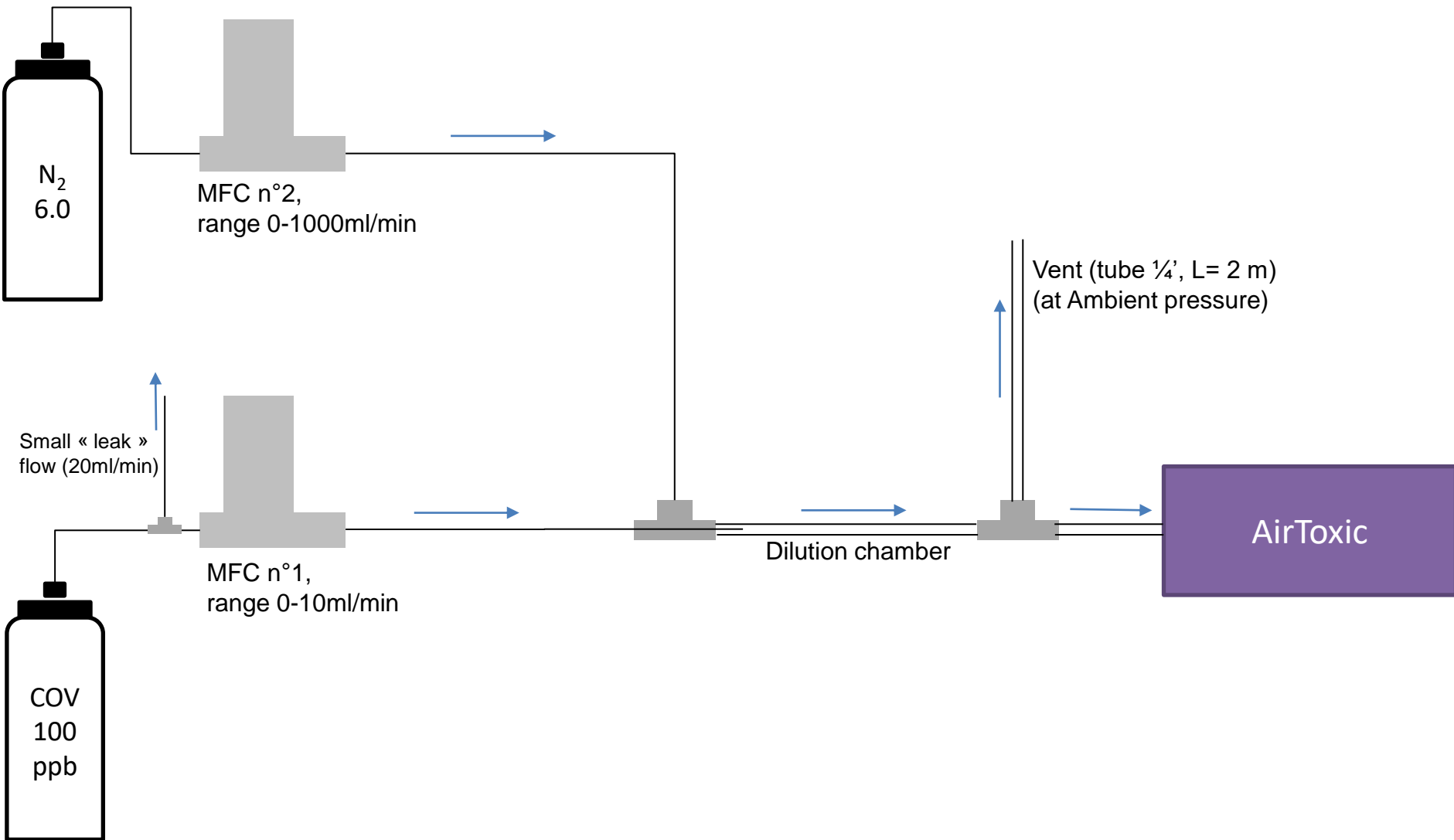
- How to verify the uncertainty is less than 1,5%?
- What kind of tests allows us to quantify this uncertainty?
- What kind of instrument using to quantify this uncertainty?
- Do not confuse the uncertainty of the flow fixed by one MFC and the uncertainty of the whole dilution system (2 MFCs, homogeneous mixture, adsorption of the compounds on the tubes...)

Tools used by Chromatotec for the test

- Dilution system with:
 - ✓ Cylinder containing BTEX (100ppb), N₂ matrix
 - ✓ Two Mass Flow Controllers
 - ✓ MFC n°1 : Bronkhorst range 0-10mL/min
 - ✓ MFC n°2 : Bronkhorst range 0-1000mL/min
 - ✓ Carrier gas of GC : N₂ 6.0
 - ✓ Gas used for the dilution : N₂ 6.0
 - ✓ All the flows are verified using BIOS flowmeters (precision : 1% read value): two flowmeters are used : range 5-500mL/min and 50-5000mL/min.
 - ✓ The vent tube is always at ambient pressure
- Dilution chamber:
 - ✓ PTFE Tube ¼'
 - ✓ Stainless steel fittings
 - ✓ Length = 20cm
 - ✓ “special mixing “Te” connector:



Tools used by Chromatotec for the test



Precautions to take before starting the test

Concerning the dilution system:

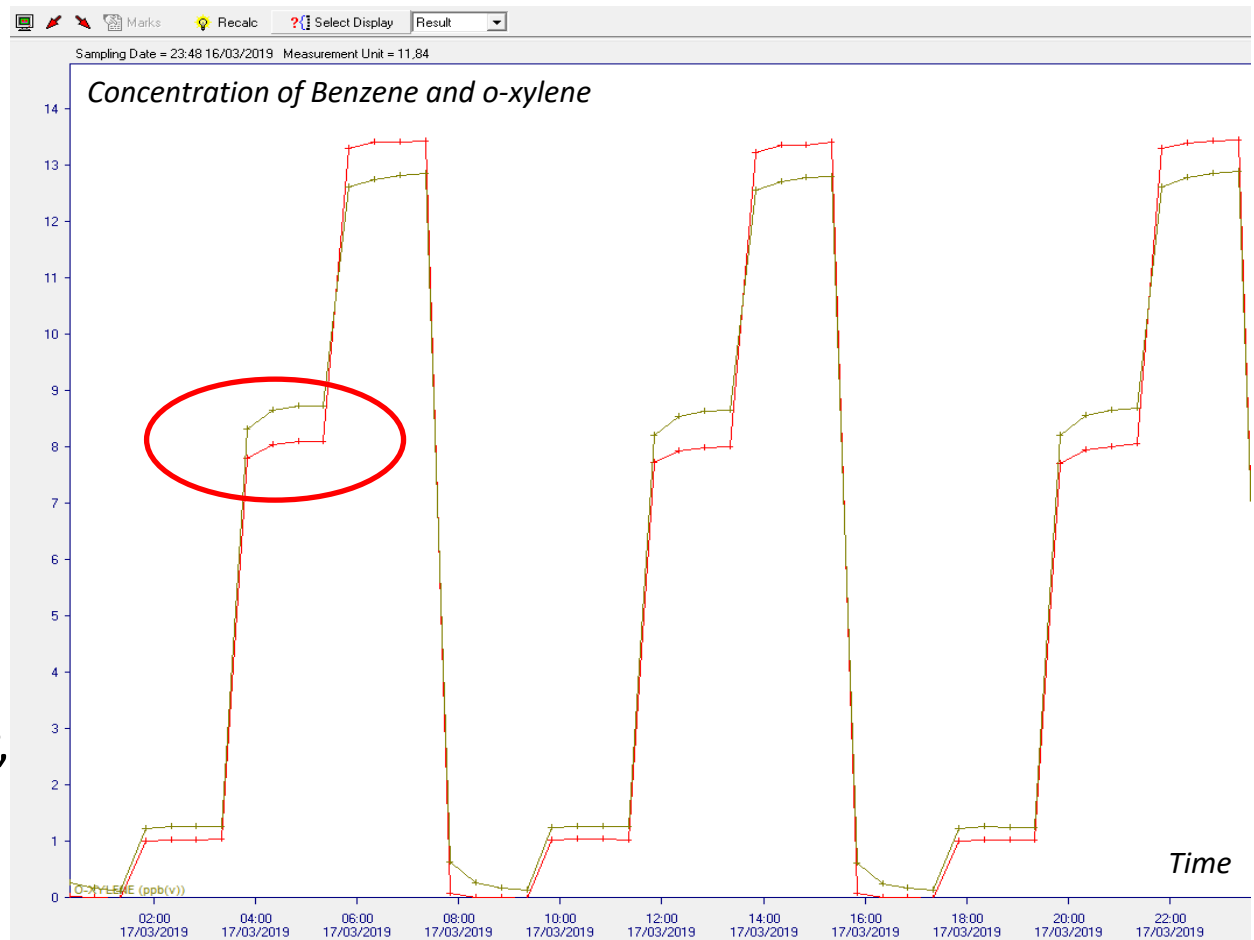
1. Flows have to be in the range of each MFC : $10\% < \text{flow} < 90\%$ to have a good regulation.
2. The gas pressure feeding each MFC has to be perfectly stable, to have a stable flow at the MFC outlet.
3. Purge the VOC cylinder 3 times before connecting it to the MFC
4. If you use gas generator for the dilution, add a pressure regulator before the MFC to optimize the flow stability on the MFC
5. Use a "leak" flow of pure VOC gas (around 20mL/min), just before the MFC n°1 to reach a stable mixture quickly
6. Do not use flows bigger than 1.5L/min at the dilutor outlet to ensure a perfect mixture
7. Check carefully the pressure at the sampling point is always at ambient pressure (check Ambient pressure displayed on Vistachrom), even for the strongest dilutions applied (with the highest flows).
8. During this test, be aware of the unit used :
Flows always displayed in the same unit on your flowmeter (mL/min standard conditions,...)
Conversion mg/m³ into ppb(v) always done with the same molar volume (at 20°C, 1013hPa)
9. During your dilution, check that for one dilution point, the concentrations used are stable (more explanations on the next slide)

Precautions to take before starting the test

- Number of repetitions for each dilution point:
All the diluting system needs time to reach a stable state : homogeneous mixture, passivation of the tubes... This time (only caused by the diluting system) must not impact negatively the tests relative to the GC linearity.

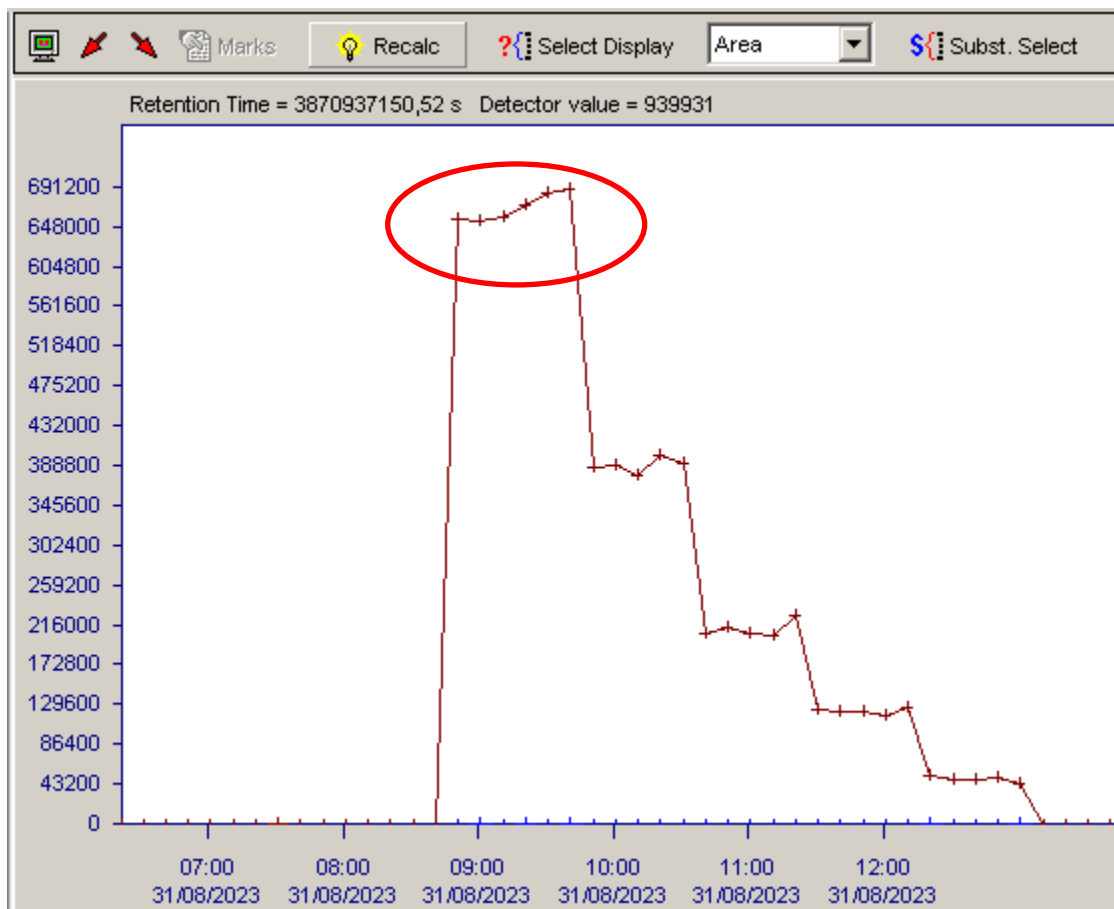
- A classic result often obtained:

⇒ Phenomenon mainly created by the dilutor, not the GC!



Precautions to take before starting the test

- Calibration mixture not stable :



Precautions to take before starting the test

- Number of repetitions for each dilution point:

Description of the test, written in the Norm :

*“For each concentration (including zero), **at least** four individual measurements have to be done. The first measurement of each series must be excluded from the calculation of the regression function.”*

Advices :

- Do more cycles for each concentration.
- Do not consider the first chromatograms obtained. Consider only the last chromatograms
- Example : in the Mcerts test, 6 cycles (30min for one cycle) were started, only the last 4 cycles were considered

